Pulsed-Laser Photochemistry of Pentanal at 355 nm

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Abstract Pure pentanal is irradiated with a frequency tripled Nd-YAG laser in the intensity interval 0.1-1 MW cm⁻² Alpha-dione and α -ketol are formed selectively with quantum yields of 5.5 and 38%, respectively As only the S₁ state of the pentanal is excited, the results obtained are explicable as a dynamic effect in connection with the order of the reactions

In UV photochemistry, aliphatic aldehydes lead to three primary processes of evolution¹² decarbonylation with the formation of hydrocarbons and cleavage reactions in α or β to the carbonyl, of type Norrish I or II Moreover, autoinhibition reactions generate RCHOH + RCO^{1 or 3} radicals which are at the basis of the formation of compounds that are either monofunctional of oxydoreduction or bifunctional of condensation such as α -diketones, α -ketols, α -diols³⁴⁵

It appeared useful to explore the synthesis of these condensation products by substituting UV lasers for the mercury lamp previously used. The specific characteristics of lasers give hope of an original behavior, particularly with regard to selectivity and quantum yield. The latter can be determined with accuracy on account of the precise knowledge of the number of photons absorbed, thanks to the geometry of the beam.

To enable us to compare the results at weak and strong intensities, we used a continuous Ar⁺ laser (351 nm) and a frequency tripled Nd-YAG laser (355 nm) The beams are used without focalisation. The light intensity with the continuous laser is 100 W cm⁻² (section ~ 1 mm²) and the peak intensity with the pulsed one varies from 0.1 to 1 MW cm⁻² (section ~ 0.5 cm²). The wavelengths of these two lasers allow population of the nn^{*} state of the carbonyl compounds

The irradiated aldehyde is n-pentanal, used pure to favour the formation of duplication products ($c = 9.4 \text{ M}^{-1}$) Moreover, by operating with the pure product, the low value of ε ($\varepsilon_{351} \equiv 0.03$ and $\varepsilon_{355} \cong 0.02$ mole ¹ cm⁻¹ *l*) is compensated for by a high concentration leading to a notable absorption for a path of a few centimeters

The structure of the products is checked using GC/MS and GC/IRFT couplings The quantitative determination of the products formed is realized by GC using diglyme as an internal standard

On operation with the continuous laser, all the substances produced by irradiation at 313 nm with a mercury vapour lamp^{2,5}, except certain products of β -cleavage, are obtained For the condensation products, the quantum yields (%) are RCOR (0.54), RCHOHR (0.53), RCOCOR (1.08), RCOCHOHR (14), RCOC₃H₅ (1.4) with R = C₄H₉

Irradiation with the pulsed laser leads essentially to the observation of two condensation products 5,6-decanedione (C₄H₉COCOC₄H₉) and 5-hydroxy 6-decanene (C₄H₉CHOHCOC₄H₉). The other products which were observed previously including the α -diol appear only in traces. This remarkable selectivity is accompanied by an increase in the quantum yields for the α -dione and the α ketol, which remain constant, allowing for uncertainty in measurement, in the interval of intensity explored, and are respectively equal to 5.5 and 38%. Transformation of pentanal into the α -ketol leads to a relative concentration of the latter of the order of 1.5% in one hour of irradiation at 1 MW cm⁻² (volume irradiated ~ 3 cm³).

The intensity required to saturate the transition $S_0 \rightarrow S_1$ may be calculated by the classical formula $I_S \sim \frac{h\nu}{\sigma\tau} = 2.61 \ 10^{20} \ \frac{h\nu}{e\tau}$ where σ is the excitation cross-section of the S_1 state and τ the lifetime of this state With $\tau \leq 1.5 \ ns^5$ one obtains $I_S \sim 5.10^{12}$ W cm⁻² This is much higher than the values of the range explored with the pulsed laser (0.1-1 MW cm⁻²) In these conditions, absorption of pentanal starting from the ground state can sull be described by the Beer-Lambert law leading to an absorbance value of 0.564 with the irradiation cell used ($l = 3 \ cm$) Direct calculation from the incident transmitted and reflected intensities measurements, performed at the beginning of the irradiation to avoid the absorption specific to the products formed, leads to almost the same result (0.559). It can be deduced that the disappearance of photons in the light beam is essentially governed by the interophotonic absorption of the pentanal, to the exclusion of multiphotonic absorptions by the latter or of absorptions by reactive species deriving from it

A fortiori, the excitation mechanism with the continuous Ar^+ laser is also limited to the monophotonic absorption of the pentanal

Being very far from saturation, the instantaneous reactive species concentrations obtained with the pulsed laser are much higher than those obtained with the continuous laser. Thus reactions of the highest order are favoured with the former as has already been noted⁶. It is no doubt this dynamic aspect of the reactions that explains our observations. In this hypothesis the quantum yields for the α -dione and the α -ketol must increase with intensity as long as the other photochemical products are still present in appreciable quantities. It is no more the case with the pulsed laser where these products appear only in traces

Study of other aliphatic aldehydes is under current investigation. In particular, the behavior of butanal is quite similar to that of pentanal

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